

## Lecture 2

### Electrochemical Cells – Definitions and Principles

*Keywords: Electrodes, Cells, Liquid Junction.*

#### Definitions and types of electrochemical cells.

Electrode: An electric conductor, the electrode metal and an ionic conductor, electrolyte solution, form an interface at which electrode process occurs. An electrochemical cell contains two electrodes (anode and cathode); a liquid-liquid junction separates two electrodes.

Anode is the electrode where oxidation occurs.

Cathode is the electrode where reduction occurs.

#### Types of electrodes:

Metal – Metal ion	$\text{Cu} / \text{Cu}^{++}$
Ion – Ion (redox)	$\text{Pt} / \text{Fe}^{+++}, \text{Fe}^{++}$
Gas	$\text{Pt} / \text{H}_2, \text{H}^+$
Metal – insoluble salt	$\text{Hg} / \text{Hg}_2\text{Cl}_2 / \text{KCl}$

**Liquid Junction:** Serves as galvanic contact between electrodes (can be a salt bridge or porous membrane). Salt bridge, very commonly used – an intermediate compartment filled with saturated KCl solution and fitted with porous barrier at each end or agar solidified incorporating saturated KCl. Salt bridge minimises liquid junction potential (diffusion potential) that develops when any two phases such as two solutions are contacted each other. This potential (if not corrected) introduces

errors and interferences in the measured cell potentials. With introduction of a salt bridge, two liquid junction potentials are created; but they tend to cancel each other (Fig.2.1).

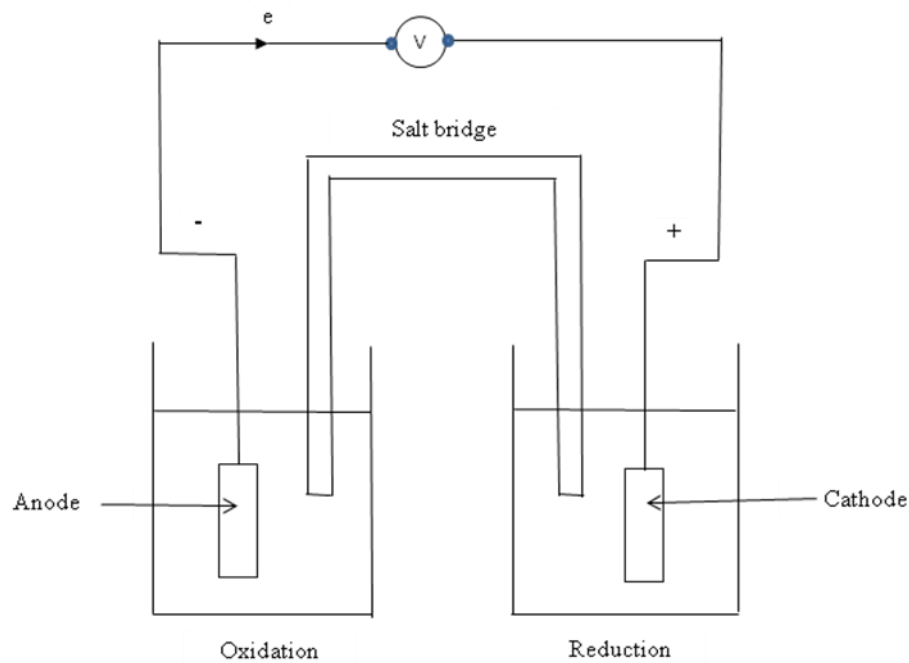


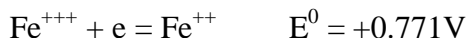
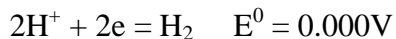
Fig.2.1 Electrochemical cell with salt bridge

### IUPAC sign convention for electrode potentials

Sign of the electrode potential,  $E^0$

- is positive when the half – cell is spontaneous as cathode.
- is negative when the half – cell behaves as anode.
- is a measure of the driving force for the half – reaction.

$E^0$  is referenced to standard Hydrogen Electrode.



$E^0$  is independent of number of moles of reactant or product.

Positive means reaction is spontaneous with respect to Hydrogen electrode.

In accordance with the recommendations of IUPAC, the present practice is to use reduction potentials.

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$$

Standard hydrogen electrode (SHE) is the reference point.

### Types of electrochemical cells

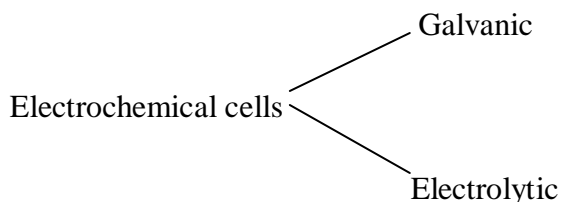


Table 2.1 Comparison of galvanic and electrolytic cells

Galvanic	Electrolytic
Chemical energy to electrical energy	Electrical to chemical energy
Spontaneous/Reversible/Thermodynamic	Non spontaneous/Kinetic cell / irreversible
Cathode (+)	Cathode (-)
Anode (-)	Anode (+)
$\Delta G^0 < 0, E^0_{\text{cell}} > 0$	$\Delta G^0 > 0, E^0_{\text{cell}} < 0$
Eg: Dry cell Daniel cell	Eg: Electroplating, Impressed current cathodic protection

## Definition of electrochemical cell

Electrodes (anode, cathode) in the presence of electrolyte. Driving force for electrochemical reaction is the potential difference between the electrodes,  $E_{\text{cell}}$ .

$$\Delta G = -nFE_{\text{cell}}$$

$n$  = moles of electrons in half reaction

$$F = 96500\text{c}$$

$$\Delta G^0 = -RT \ln K$$

Nernst relationship:

$$E = E^0 + \frac{RT}{nF} \ln \frac{a_{\text{Ox}}}{a_{\text{Red}}}$$

$$E_h = E^0 + \frac{RT}{nF} \ln \frac{[\text{Ox}]}{[\text{Red}]}$$

$$E_h = E^0 + \frac{0.059}{n} \log \frac{[\text{Ox}]}{[\text{Red}]} \text{ at } 25^0\text{c}$$

Where  $E^0$  is the standard electrode potential,  $\frac{[\text{Ox}]}{[\text{Red}]}$  is the ratio between activities of oxidized and reduced species.

**Daniel cell** is an example of a galvanic cell - contains zinc immersed in zinc sulfate solution and copper in copper sulfate solution separated by a diaphragm or salt bridge (Fig. 2.2).

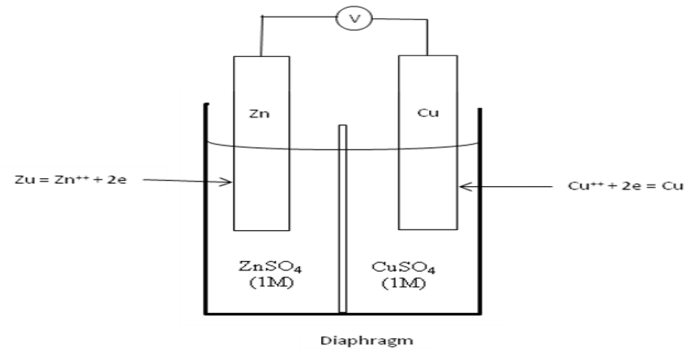


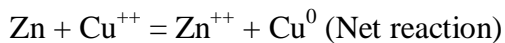
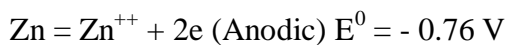
Fig.2.2 Diagrammatic representation of Daniel cell



+ Right Rule

$$E_{\text{cell}} = E_{\frac{1}{2}(\text{Right})} - E_{\frac{1}{2}(\text{Left})}$$

The sign of cell reaction potential ( $E_{\text{cell}}$ ) should be positive indicating spontaneous reaction. Single vertical line denotes electrode – solution interface. Double vertical lines in the middle indicates liquid junction is eliminated.



Zinc ions enter the aqueous phase leaving two electrons behind. (oxidation, polarity of anode is negative): copper ions deposit by taking up two electrons (reduction, polarity of cathode is positive).

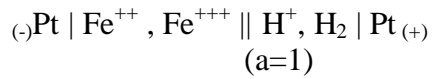
at 1M concentration for  $\text{Zn}^{++}$  and  $\text{Cu}^{++}$

$$E_{\text{cell}} = +0.34 - (-0.76) = +1.1\text{V}$$

The cell is spontaneous

For the reaction,  $\text{Fe}^{++} = \text{Fe}^{+++} + e$

$$E_h = 0.771 + 0.059 \log \left[ \frac{\text{Fe}^{+++}}{\text{Fe}^{++}} \right]$$



For the reaction  $2\text{H}^+ + 2e = \text{H}_2$

$$E_h = 0 + \frac{0.059}{2} \log [\text{H}^+]^2$$

at  $\text{pH}_2 = 1$ ,  $E_h = 0 - 0.059 \text{ pH}$